Enhanced biomass characterization: A Foster Wheeler Energy Corporation/ Penn State initiative

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Introduction

Foster Wheeler Energy Corporation is undertaking a major fuel evaluation program, including all ranks of coal, petroleum coke, tires, and biomass materials, to develop new fuel standards. Most of the existing fuel standards are based upon eastern and Midwestern bituminous coals and do not represent the full range of solid fuels available. These techniques are typically old and have been developed based upon stoker firing and do not represent conditions of other boilers. Several modern techniques, such as thermal gravimetric analysis (TGA), are semi-quantitative and need amplification for quantitative analysis. None of the techniques provide information for improving NO_x control and unburned carbon loss (LOI).

Penn State's The Energy Institute assisted Foster Wheeler in developing a program to characterize both the organic and inorganic portions of the fuels, identify nitrogen species evolving during pyrolysis, and determine the kinetics of pyrolysis and char oxidation. As the project progresses, expected relationships to be developed include: maceral analysis and aromaticity; proximate analysis and devolatilization yields; aromaticity and kinetics; oxygen functionalities and kinetics; devolatilization and char oxidation kinetics as related to traditional analyses; nitrogen structure and volatiles evolved; and nitrogen structure, coal structure, and fate of nitrogen to char and to various species.

In this paper, the characterization of two biomass samples, sawdust and switchgrass, will be presented. The methods used in the characterization will be discussed and a summary of the results will be presented and compared to published data, when available.

Characterization Methods Used

The characterization of the fuels in the Foster Wheeler test program is divided into three broad categories: 1) composition and structure; 2) reactivity measures; and 3) ash chemistry. The analyses employed to determine composition and structure include:

- Basic analyses including proximate and ultimate analysis and calorific value;
- Maceral analysis (coals only);
- Cellulose/ lignin content; oxygen functionality and aromaticity using CP/MAS ^{13}C NMR; and
- Nitrogen functional groups using ^{15}N NMR.

The analyses employed to measure reactivity include determining the:

- Volatile matter/ fixed carbon split over a range of temperatures (800-1,700°C);
- Devolatilization kinetics using a drop-tube reactor (DTR);
- Char oxidation kinetics using a TGA;
- Reactivity constants using a TGA;
- Nitrogen volatiles evolved from the DTR using GC-NPD and GC-TCD; and
- Nitrogen remaining in the char from the DTR tests.

The ash chemistry of the fuels includes determining elemental composition, slagging and fouling characteristics, and the mode of occurrence of the mineral matter in the fuels.

Details of the analytical techniques used to characterize the sawdust sample will be discussed in the paper.

Summary of Results

A sawdust sample from Allegheny Energy's Willow Island cofiring demonstration has undergone the full suite of analyses discussed in the previous section. The sawdust is a blend of material received from various suppliers for the demonstration. Testing has also started (as of March 2001) on a switchgrass sample obtained from Southern Research Institute and the results will be presented in the paper.

Composition, Structure, and Ash Chemistry: The analysis of the sawdust, which contained an as-received moisture content of 42 wt.%, is given in Table 1. Results from chemical fractionation of the sawdust sample will be discussed in the paper.

Table 1. Analysis of the Willow Island Sawdust and Ash Composition

Fuel Composition		**Ash Constituent**	***(wt.%, reported on an oxide basis)***
Proximate Analysis	***(wt.%, dry basis)***	LOI (900°C)	32.1
Volatile Matter	80.05	Al_2O_3	1.56
Fixed Carbon	18.97	BaO	0.32
Ash	0.98	CaO	62.0
		Fe_2O_3	1.88
Ultimate Analysis	***(wt.%, dry basis)***	K_2O	15.0
Carbon	49.20	MgO	2.18
Hydrogen	5.99	MnO	1.57
Nitrogen	0.82	Na_2O	0.61
Sulfur	0.03	P_2O_5	1.23
Oxygen	42.98	SiO_2	9.44
Ash	0.98	SrO	0.15
		TiO_2	0.10
HHV *(Btu/lb)*	8,414	SO_3	2.72

The oxygen functional groups and aromaticity of the sawdust were determined. The sawdust sample was analyzed by CP/MAS ^{13}C NMR spectroscopy employing a contact time of 1 ms and recycle delay of 1 s. The primary constituent was found to be cellulose as determined by characteristic bands at 103 and 72 ppm. The aromaticity of the Willow Island sawdust was measured to be 0.08, which is representative of the lignin component of the sample.

Reactivity and Nitrogen Speciation: Penn State's DTR was used to generate char samples at temperatures ranging from 600 to 1,700°C. The devolatilization kinetic parameters were calculated based on the rate of weight loss as a function of temperature. The pre-exponential factor, A, and apparent activation energy, E were determined. In addition, gas samples were collected during the DTR tests and analyzed by GC-NPD and GC-TCD for nitrogen speciation; however, due to the low nitrogen content in the fuel, no species were detected.

Char samples generated under high temperature heating conditions in the DTR were used to determine char oxidation kinetics using a Perkin Elmer TGA. The char reactivity was determined at four temperatures (350, 375, 400, and 425°C). The weight loss curves were obtained and the rate constants were calculated using Arrhenius plots.